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GAS CHROMATOGRAPHIC ANALYSIS OF HYDRAZINE, MONOMETHYLHYDRAZINE AND WATER IN MIXED HYDRAZINE FUELS (U)

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(10) Richard M. Jones
Propulsion Development Department

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ABSTRACT. A gas chromatographic procedure is described for the analysis of a mixture of hydrazine, monomethylhydrazine (MMH) and water (17) RMMP 24/080/216 FOC9/060/02

Analyses were obtained by the use of a Perkin-Elmer Vapor Fractometer Model 154-C with a Leeds and Northrup recorder and an Instron integrator. A column packed with 10 percent Dowfax 9N9 on Teflon 6 was used. The elution of the peaks required about 7 minutes and the peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within ± 0.5 percent of the amount of the individual components present in a synthetic mixture. The synthetic mixture was prepared from materials which had been analyzed by the acidimetric method. (UNCLASSIFIED)

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FOREWORD

During the applied research stage of the development of liquid propellant systems it was necessary to develop a rapid and accurate analytical procedure for the determination of the composition of mixed hydrazine fuels (hydrazine, MMH, and water).

There are many procedures for the analysis of mixtures of hydrazines but they were found to be inadequate when used for analysis of hydrazine –MMH compositions because they did not separate these components adequately for the accurate analysis required for use with rocket fuels.

The presented gas chromatographic procedure is simple, rapid, and accurate to within ± 0.5 percent.

This report was reviewed for technical accuracy by Dr. W. R. Carpenter and E. M. Bens. The work was performed under BuWeps Task No. RMMP-24-080/216-1/F009-060-02.

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NEGATIVE NUMBERS OF ILLUSTRATIONS

FIG. 1, LHL 106216; FIG. 2, LHL 105476; FIG. 3, LHL 105750; FIG. 4, LHL 105477; FIG. 5, LHL 105478.

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The author is indebted to Dr. W. R. Carpenter and E. M. Bens of the Research Department for their assistance and advice in the development and evaluation of this chromatographic procedure.

INTRODUCTION

Hydrazine and monomethylhydrazine (MMH), being chemically similar and highly reactive compounds, have been difficult to analyze when present in the same mixture. There are many procedures available for the determination of water in hydrazines (Ref. 1, 2, and 3). There are a few gas chromatographic procedures in use for mixtures of hydrazine, MMH, and water; however, these procedures were found to be complicated and lengthy and without the accuracy required for the analysis of rocket fuels. The hydrazines, because they are strong bases and reducing agents, cause deterioration of the column material resulting in poor column stability.

The method of chromatographic separation of mixtures containing hydrazine, MMH, and water described in this report utilizes a column of 10 percent Dowfax 9N9, a product of Dow Chemical Company, Midland, Michigan, on Teflon 6, a product of E. I. duPont deNemours and Company, Inc., Wilmington, Delaware. This procedure was adapted from a description of the separation of amines and amides with Dowfax 9N9 as the liquid phase (Ref. 4 and 5). This procedure as developed for analysis of mixed hydrazine fuels of hydrazine, MMH, and water proved simple, rapid, and accurate with excellent column stability.

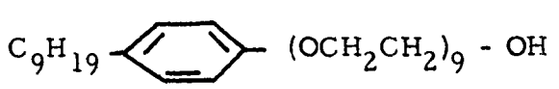
EXPERIMENTAL

APPARATUS

All analyses were performed with a Fractometer (Perkin-Elmer Corp., Norwalk, Connecticut, Model 154-C Vapor Fractometer) using a dual chamber thermistor thermal conductivity cell. Chromatograms were recorded on a 5 millivolt (mv) full scale recorder (Leeds & Northrup Co., Philadelphia, Pennsylvania) at a chart speed of 1/2 inch per minute. An Instron integrator, two-counter model (Instron Engineering Corp., Canton, Massachusetts) was used to integrate the eluted peaks (Fig. 1).

COLUMN PREPARATION

The column materials were Dowfax 9N9 and Teflon 6. The chemical composition of Dowfax 9N9 is:



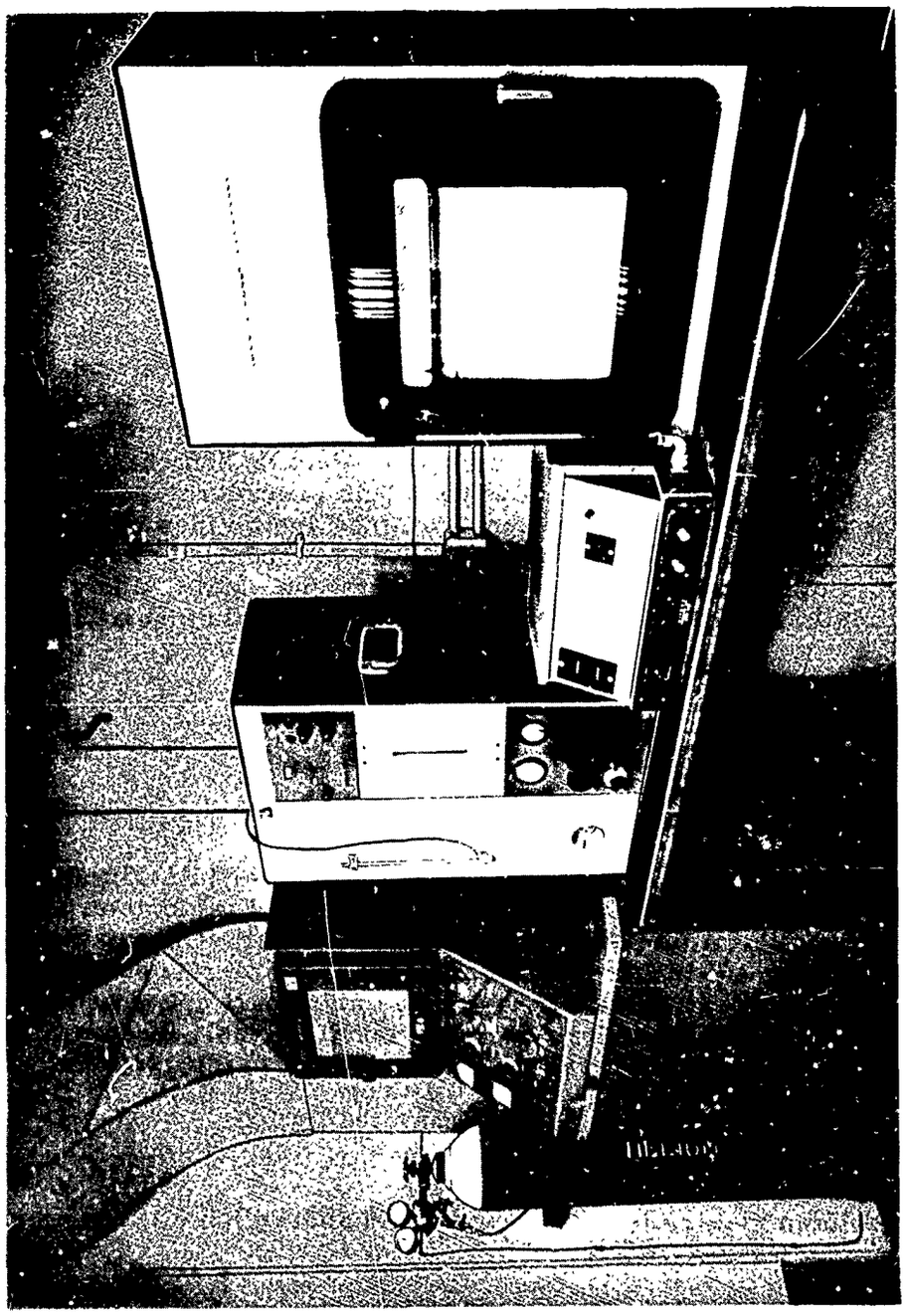


FIG. 1. Gas Chromatograph and Equipment.

The column was prepared by air drying a slowly stirred slurry of Dowfax 9N9 and Teflon 6 in methanol in amounts necessary to produce a 10 percent Dowfax 9N9 coating. The material was further dried in a vacuum oven at 100°C, chilled, screened through a 30-mesh sieve and carefully packed into a 6-foot stainless steel tube, 1/4-inch outside diameter (OD). The packing weight was about 22 grams. The column was then stabilized overnight at 150°C with a 20 milliliter (ml) per minute helium flow rate. The column was then conditioned to each day's use by one or more injections of about 10 $\mu\ell$ of hydrazine.

SAMPLE PREPARATION

The known composition mixtures were prepared from hydrazine and MMH materials from Olin Chemical Co., Lake Charles, Louisiana. The hydrazines were purchased in accordance with Military Specifications (Ref. 6 and 7).

Samples of hydrazine and MMH were analyzed by the acidimetric method (Appendix A and Ref. 8). Analyses of 97.0 ± 0.2 percent hydrazine and 90.9 ± 0.2 MMH were obtained. These samples were used for the preparation of the first known composition mixtures. Later analyses were made of samples from a new supply; the results were 98.6 ± 0.2 percent hydrazine and 99.4 ± 0.2 percent MMH. These materials were used for the preparation of MHF-3, Bell Aero Fuels (BAF) (Bell Aero Systems, Inc., Buffalo, New York) and the typical mixture.

The known composition mixtures were prepared by adding different weighed amounts of water to hydrazine and to MMH and by mixing hydrazine, MMH, and water in various percentages (see Table 1).

ANALYTICAL PROCEDURE

The separation of hydrazine, MMH, and water was obtained by injection of a sample of approximately 5 $\mu\ell$ using a Hamilton 10 $\mu\ell$ microsyringe. The attenuation settings were determined from the estimated sample percent composition. A column temperature of 110°C and a helium flow rate of 40 ml per minute were maintained. All the peaks were eluted after about 7 minutes. An additional 10 minutes was allowed before the next analysis to let the baseline stabilize. The procedure is described in Appendix B.

TABLE 1. Percent Composition and Reciprocal Response Ratios of Water to Hydrazines

Sample	Percent component			Ratio H_2O = 1	
	MMH	H_2O	N_2H_4	H_2O/MMH	H_2O/N_2H_4
1	...	1.36	98.64	...	0.74[a]
2	...	2.97	97.03	...	0.56[a]
3	...	11.50	88.50	...	1.05[a]
4	...	30.64	69.36	...	1.06[a]
5	...	50.49	49.51	...	1.04[a]
6	99.36	0.64	...	1.03[b]	...
7	90.85	9.15	...	0.67[b]	...
8	83.41	16.59	...	1.15[b]	...
9	64.24	35.76	...	1.17[b]	...
10	45.65	54.35	...	1.20[b]	...
11	27.57	72.43	...	1.18[b]	...
12	14.46	3.77	81.77	0.60	0.68
13	25.53	4.55	69.92	0.69	0.80
14	29.13	4.80	66.07	0.59	0.60
15	45.89	5.98	48.13	0.65	0.60
16	53.08	6.49	40.43	0.68	0.61
17	68.73	7.58	23.69	0.68	0.55
18	80.88	8.45	10.67	0.72	0.53
19	85.47	0.75	13.78	1.35	1.19
20	40.36	25.00	34.64	1.24	1.18
21	48.67	20.86	30.47	1.29	1.22

[a]Ratio of water to hydrazines for samples 1 through 5 were used in Fig. 2.

[b]Ratio of water to MMH for samples 6 through 11 were used in Fig. 2.

CALCULATIONS

The relative response ratio method of calculating percent composition of samples was used in this study. This method of determining percent composition was used because of its accuracy and property of being independent of variations in temperature, sample size, carrier gas flow rate and type of thermal conductivity detector used (Ref. 9 and 10).

The relative response of each component compared to water was determined from mixtures of known composition of the hydrazines and water. To simplify the calculation of reciprocal response ratios, the reciprocals of the relative response ratios were employed. These reciprocal response ratios were then used to calculate the composition of samples being analyzed. The reciprocal responses were calculated from the formula:

$$R = \frac{CA}{W}, \quad r_h = \frac{R_w}{R_h}, \quad r_m = \frac{R_w}{R_m}, \quad r_w = 1 \text{ by definition}$$

where:

R = response

C = integrator counts

A = attenuation

r = reciprocal response ratio

h = hydrazine

m = MMH

w = water

W = weight

The reciprocal responses are shown in Table 1 and Fig. 2. These ratios were determined from an average of at least three analyses. The percentage compositions were calculated by the following formula, which is given in this case, for hydrazine.

$$\% \text{ hydrazine} = \frac{C_h A_h r_h \times 100}{C_h A_h r_h + C_m A_m r_m + C_w A_w r_w}$$

Analogous formulas were used for other components.

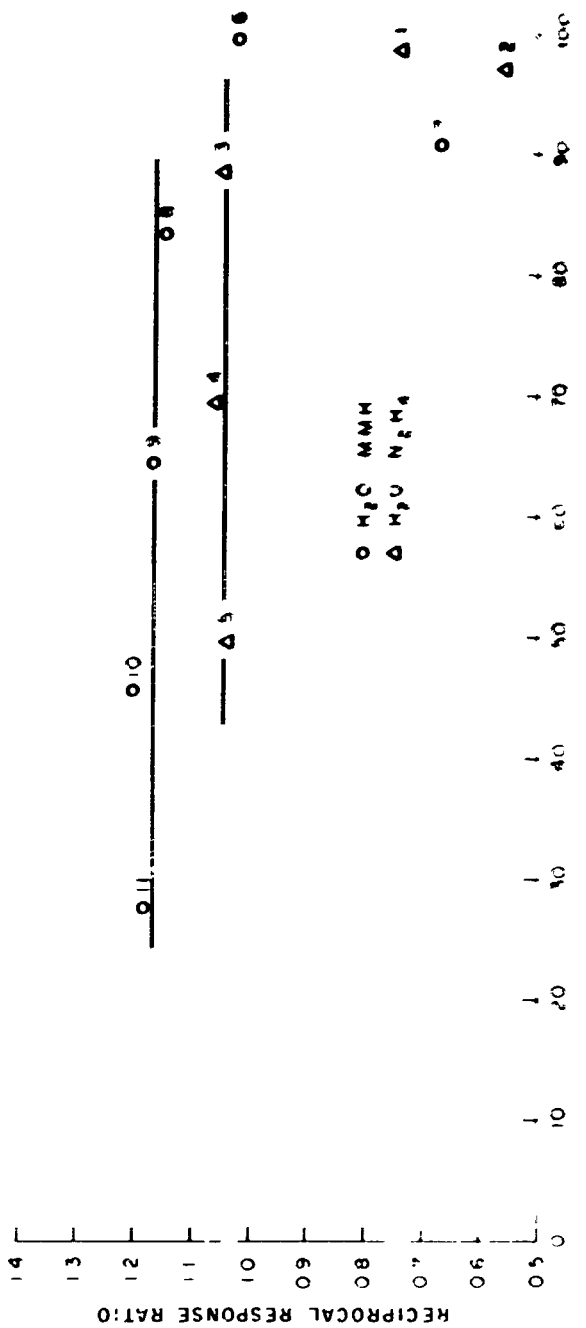


FIG. 2. Reciprocal Response Ratios of Water to Hydrazine.

The calculated responses were based on prepared mixtures of known composition and depend on the acidimetric analysis of the hydrazine and MMH which is accurate to about ± 0.2 percent.

DISCUSSION

An acidimetric analysis was used for the assay of the original hydrazine and MMH materials because the procedure is simple, rapid and the degree of accuracy is adequate, if impurities which are basic in reaction are not present in significant amounts. The iodimetric method (Ref. 8) was used as a check of the acidimetric procedure to determine the level of basic nonreducing impurities, which would interfere with the calculations. Since this method duplicated the acidimetric analysis of the hydrazine and gave values of 3 to 4 percent higher in the MMH analysis, it indicated that the basic nonreducing impurities were not present in significant amounts. The gas chromatographic analysis indicated that the acidimetric analysis of MMH was more accurate than the iodimetric method.

In Table 1 and Fig. 2 the reciprocal response ratios showed only slight variations with changes in water down to the 10 percent level. Below this, small errors in the calculated amount of water created large errors in the calculated reciprocal response ratios.

It is apparent that in the region of from 2 to 10 percent water the reciprocal response ratios for both hydrazine and MMH are low; however, below 2 percent water these ratios become higher. Nevertheless, these values still give calculated percent compositions which compare favorably with acidimetric analysis because errors involved only a small percentage of the sample.

Correspondence from G. D. Lake, AFPCL, Vandenberg AFB, California and the Olin Chemical Co. stated that they were using a Fractometer with a column of 15 percent triethanolamine on potassium hydroxide (KOH) washed Chromosorb W. The author prepared a similar column which proved to be adequate and did separate unsymmetrical dimethylhydrazine (UDMH) from hydrazine, MMH, water mixture (Fig. 3). This column had the disadvantages of long retention for the hydrazine, rapid column fatigue and incomplete separation of water and MMH.

The attenuations for the triethanolamine column using about a $\mu\ell$ sample were 32X, 16X, 16X, and 8X for UDMH, water, MMH, and hydrazine, respectively (Fig. 3).

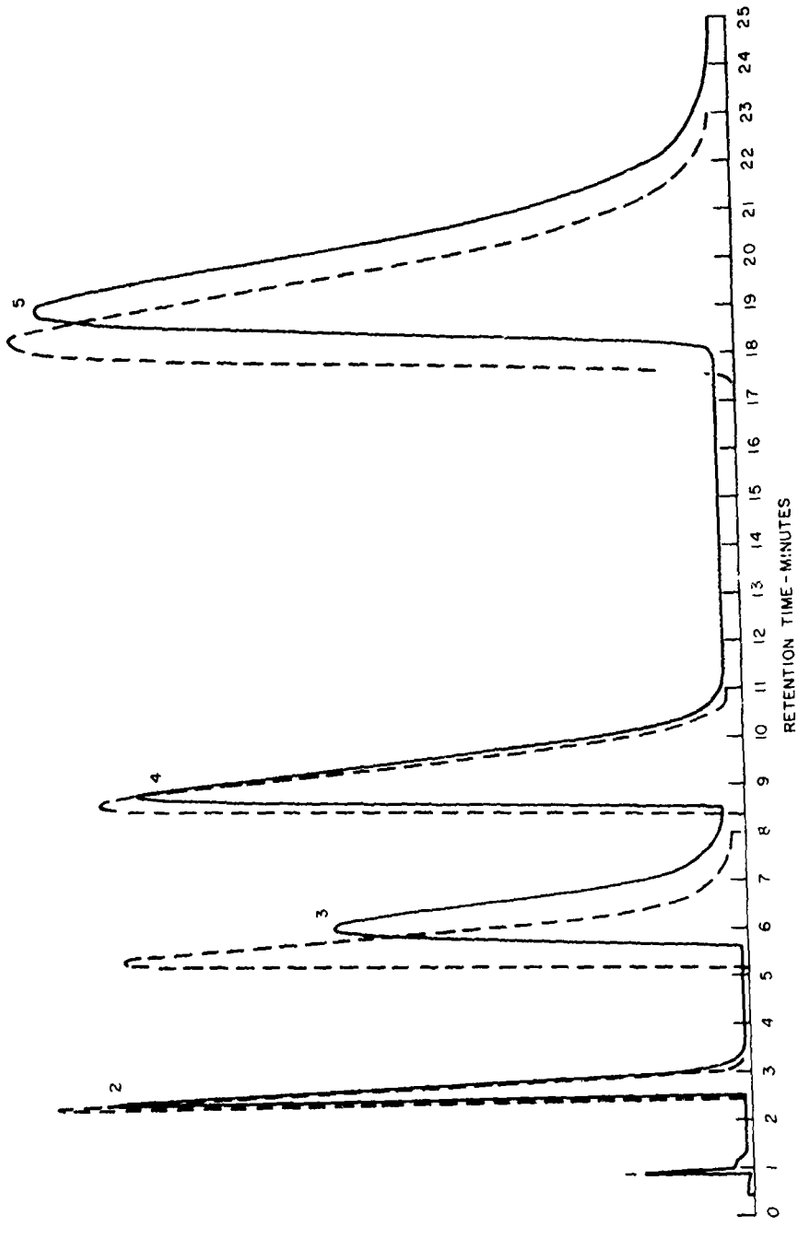


FIG. 3. Resolution of a Typical Mixture of Hydrazines and Water by 15 Percent Triethanolamine on KOH Washed Chromosorb W.

Identification of Peaks: 1. Air, 2. UDMH, 3. Water, 4. MMH, 5. Hydrazine.
-- Individual component run.
— Mixed component run (16.6% UDMH, 24.6% Water, 31.9% MMH, 26.9% hydrazine).

The Bell Aero Systems, Inc., in correspondence, stated they were using dual columns of 15 percent tetrahydroxylethylenediamine (THEED), 15 percent Carbowax 400 on Chromosorb W (60 to 80 mesh) with a program temperature control. They stated that this column required about 30 minutes elution time. Since no chromatogram was shown, the degree of separation could not be determined.

In the proposed Military Specification for MHF-3 (Ref. 11) a 30 percent Quadrol, N, N, N', N' - tetrakis (2 hydroxypropyl) ethylenediamine on firebrick was the suggested column. Work on similar columns by E. M. Bens of the Research Department indicated poor separations and long retention times of hydrazines when compared to the Dowfax 9N9 column.

In developing a workable column for the analysis of hydrazine, MMH, and water mixtures, several columns were prepared and tested. The first was a column prepared as described in Ref. 4 with 10 percent Dowfax 9N9 and 1 percent sodium hydroxide on Chromosorb W. This column did not separate water from MMH. A second column was prepared with 10 percent Dowfax 9N9 and 1 percent sodium hydroxide on Teflon 6 (Ref. 12). This column partially separated water from MMH, but not sufficiently for good analysis. A third column was prepared as described in the column preparation section with 10 percent Dowfax 9N9 on Teflon 6 without sodium hydroxide. This column separated the three components sufficiently for good analysis with only a slight increase in hydrazine tailing. An interesting feature of this analysis was the shifting of retention times of the components depending on whether each one is injected separately or in mixtures. This anomaly is shown in Fig. 4 and 5.

The peaks were eluted in the order of air, ammonia, water, MMH, and hydrazine. The retention times were approximately 2, 3, and 4-1/2 minutes for water, MMH, and hydrazine, respectively (Table 2 and Fig. 4 and 5).

The chromatogram shows the presence of air and ammonia which could be present as an impurity in the sample or as a result of decomposition of the hydrazine upon injection into the Fractometer. This decomposition was particularly evident at a high injector temperature used in some of the early work. The injector temperature in the analysis in this study was near the temperature (110°C) of the column The amount of ammonia is small (less than 1 percent) and was found to have no significant effect on the relative response ratios.

TABLE 2. Retention Times of Hydrazines – Water Mixtures. (110°C at 40 ml/min)

Mixture	Component	Retention time, [a] min
1	Water (10%)	2.0
	MMH (90%)	3.2
2	Water (3%)	2.0
	N_2H_4 (97%)	4.4
3	Water (25%)	2.2
	MMH (40%)	3.4
	N_2H_4 (35%)	5.0
4	Water (1.6%)	2.0
	MMH (84.1%)	3.1
	N_2H_4 (14.3%)	.6

[a]Retention times measured from injection.

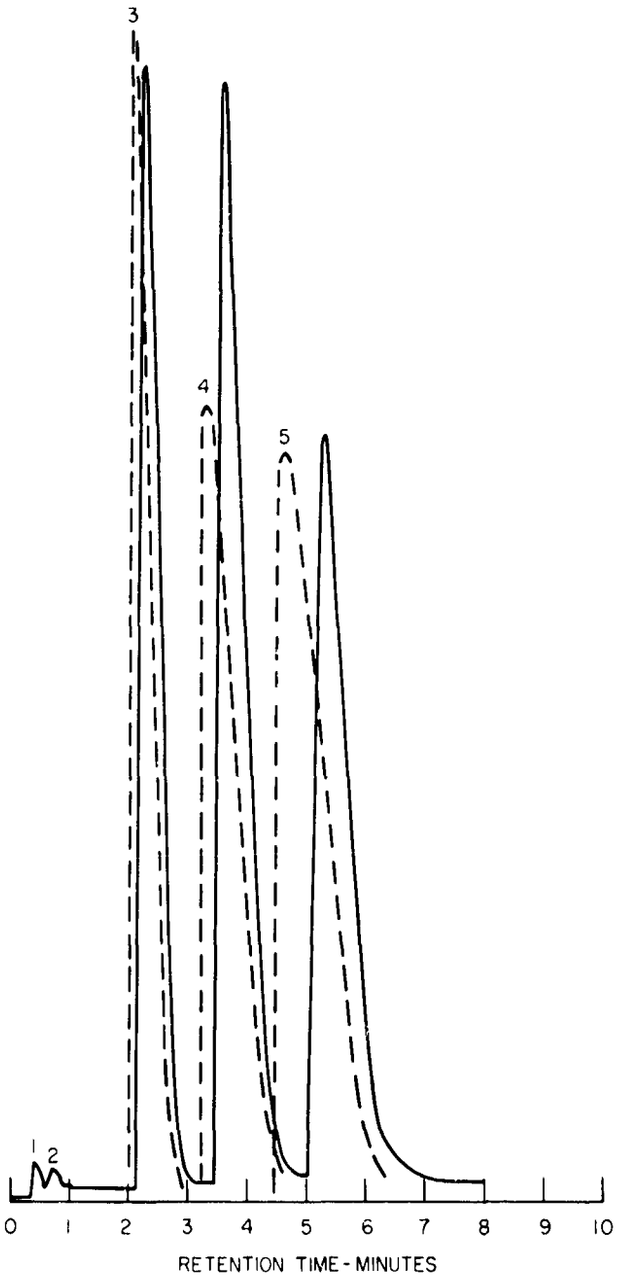


FIG. 4. Resolution of a Typical Mixture of Hydrazines and Water by 10 Percent Dowfax 9N9 on Teflon 6.

Identification of Peaks: 1. Air, 2. Ammonia, 3. Water, 4. MMH, 5. Hydrazine
-- Individual component run
— Mixed component run (25% water, 40% MMH, 35% hydrazine).

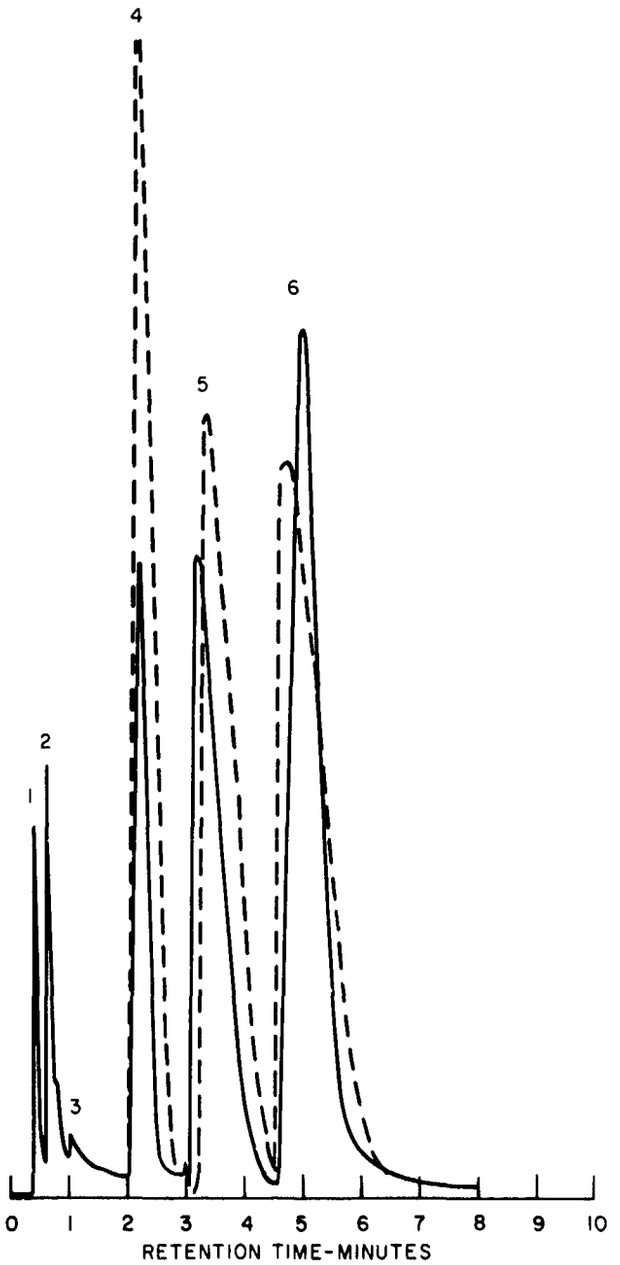


FIG. 5. Resolution of MHF-3 Fuel by 10 Percent Dowfax 9N9 on Teflon 6.

Identification of Peaks: 1. Air, 2. Ammonia, 3. Impurities, 4. Water, 5. MMH, 6. Hydrazine.
-- Individual component run
— Mixed component run MHF-3 (MAX 2% water, 86 ± 2% MMH, 14 ± 2% hydrazine)

The chromatograms of hydrazine and MMH, both individually and in mixtures at low attenuation, show an impurity peak which occurs between the MMH and hydrazine peaks. The impurity was not identified and the amount was too small to be determined at the attenuations used during the analysis. Two of the chromatograms obtained during the analysis of the mixtures are shown in Fig. 4 and 5.

A chromatogram of a typical mixture of hydrazines and water was prepared with a composition of 25.0 percent water, 40.4 percent MMH, and 34.6 percent hydrazine (Fig. 4). The attenuation setting for this mixture was at 32X for all peaks. The chromatographic analysis showed a composition of 24.3 percent water, 40.8 percent MMH, and 34.9 percent hydrazine. The reciprocal response ratios used were obtained from a prepared mixture of 20.8 percent water, 48.7 percent MMH, and 30.5 percent hydrazine. The ratios were 1:1.29 and 1:1.22 for water to MMH and water to hydrazine, respectively (Table 1).

The reproducibility of this procedure is shown in Table 3. The reciprocal response ratios used were obtained from a prepared known sample. These ratios were then used to calculate the percent composition of this same known sample in subsequent runs.

TABLE 3. Reproducibility of Analysis

Component	Reciprocal[a] response ratio	True[b] value in %	Sample determinations, % composition			Av. %	Difference, %
			1	2	3		
H_2O	1	25.00	24.98	24.90	24.95	24.94	-0.06
MMH	1.24	40.36	40.38	40.39	40.23	40.33	-0.03
N_2H_4	1.18	34.64	34.63	34.70	34.82	34.72	+0.08

[a] Reciprocal response ratios determined from the prepared mixture sample 20 Table 1.

[b] True values of the prepared mixture, sample 20, Table 1.

An MHF-3 fuel mixture prepared by the Liquid Propellants Branch was analyzed. The nominal composition of MHF-3 is 86 ± 2 percent MMH, 14 ± 2 percent hydrazine and 2 percent maximum water. The attenuations were 4X, 64X, 16X for water, MMH and hydrazine, respectively. The air and ammonia peaks were at 4X (Fig. 4). The analysis of the chromatogram (Fig. 4) showed a composition of 1.5 percent water, 84.2 percent MMH, 14.3 percent hydrazine. The relative response ratios used were obtained from a prepared mixture of 0.8 percent water, 85.4 percent MMH, 13.8 percent hydrazine with ratios of 1:1.35 and 1:1.19 for water to MMH and water to hydrazine, respectively (Table 1). These analyses were duplicated to within ± 0.5 percent.

BAF fuel mixtures of hydrazine, MMH and water were supplied by the Liquid Propellants Branch and Bell Aero Systems, Inc. This is a proprietary fuel; therefore, the composition and analysis are not available for publication. The analyses were duplicated to within ± 0.5 percent.

A number of chromatographic analyses were made on prepared samples. The statistical data indicated that 99 percent of all values collected will fall within ± 0.71 percent of the average value of three data points at the 95 percent confidence level. If the mean of three data points is used, the mean will be within ± 0.41 percent of the true value of each of the components as calculated by weight.

It has been observed empirically that the ratio of the MMH to hydrazine can vary up to 5 percent and the analysis will remain within 1 percent of the true values.

The accuracy of the chromatographic analysis ultimately depends on the accuracy of the acidimetric analysis of the hydrazine and MMH used in the preparation of the synthetic mixtures.

The 10 percent Dowfax 9N9 on Teflon 6 material was used with other instruments to determine the reproducibility of the column under different conditions. A Fractometer, using a disc integrator and a column similar to the one used in the previous analyses, was used to analyze prepared mixtures. Also an Aerograph Autoprep Model A-700 using a Royson integrator and a 6-foot coiled aluminum column 1/4-inch OD was used to analyze prepared mixtures. The results were comparable to those obtained previously and showed no greater variation than was observed in the original analysis.

A column was used for approximately 200 analyses without apparent fatigue, showing excellent stability. The column should not be used for other compounds while being used for hydrazine analysis because of the highly reactive characteristics of hydrazines.

CONCLUSIONS

Statistical analysis of the data obtained from gas chromatic analysis with the Dowfax 9N9 indicates that mixtures of hydrazine, MMH, and water can be determined to within ± 0.5 percent of the true value of each component.

The 10 percent Dowfax 9N9 on Teflon 6 column has the advantage of short retention times (individual runs required approximately 7 minutes) minimal tailing, excellent resolution and column stability. It has the disadvantage of being unable to separate UDMH and water.

Appendix A

PROCEDURE FOR ACIDIMETRIC ANALYSIS OF HYDRAZINES

The acidimetric procedure (Ref. 8) for analysis of hydrazines was used to determine the percent purity of the individual hydrazine and MMH samples. This method does not analyze for mixed hydrazines except in conjunction with other methods. This method has a precision of about ± 0.1 percent, if there are no interferences from ammonia and other basic compounds.

APPARATUS AND REAGENTS

1. 0.5N hydrochloric acid (HCl) standardized with 0.5N sodium hydroxide (NaOH) standardized with potassium acid phthalate

2. Methyl red indicator in 95 percent ethanol

3. 10 ml buret

4. 1 ml tuberculin syringe with no. 27 needle

5. Distilled water, carbon dioxide (CO_2) free by boiling or bubbling with helium

6. Analytical balance

7. 250 ml beaker

PROCEDURE

1. To a 250 ml beaker containing 50 ml of distilled water, CO_2, free, titrate approximately 3 ml of 0.5N HCl. Record accurately the amount of HCl as this is used in the calculations.

2. Using a 1 ml tuberculin syringe, with the tip of the needle in the solution, measure a 0.20 to 0.25 gram sample weighed to the nearest 0.1 milligram by difference into the beaker of HCl solution. Allow the solutions to stand approximately 30 minutes. Since the solutions are acidic, the hydrazines are not reactive with oxygen or CO_2.

3. Add 10 drops of methyl red indicator and titrate to the red end point with 0.5N HCl. After 10 minutes again titrate to the red end point.

4. Calculation:

$$\% \text{ free hydrazine + basic material} = \frac{\text{ml (HCl)} \times \text{N (HCl)} \times \text{mol wt (hydrazine)}}{10 \times \text{sample weight in grams}}$$

molecular weights:

hydrazine	32.05
MMH	46.08
UDMH	60.12

Appendix B

GAS CHROMATIC PROCEDURE FOR ANALYSIS OF MIXED HYDRAZINE (HYDRAZINE AND MMH) AND WATER

This gas chromatographic procedure was developed for the analysis of some of the MHF and BAF series fuels which are mixtures of hydrazine, MMH and water. This procedure determines the percentage of each component in the mixture to an accuracy of ± 0.5 percent.

APPARATUS

1. Perkin-Elmer Model 154-C Vapor Fractometer with dual chamber thermistor thermal conductivity cell

2. Leeds and Northrup (5 mv full scale) recorder

3. Instron integrator, two-counter model

4. Hamilton microsyringe, 10 $\mu\ell$

5. Helium, tank fitted with regulating pressure gage

6. Column (6-foot x 1/4-inch OD) packed with 10 percent Dowfax 9N9 on Teflon 6.

PROCEDURE

1. The Fractometer is adjusted to a column temperature of 110°C, in accordance with the Perkin-Elmer Instruction Manual.

2. The helium flow rate is adjusted to 40 ml per minute by controlling the Fractometer pressure valve.

3. The integrator and recorder are turned on and then calibrated with the Fractometer in accordance with the Integrator Instruction Manual so that the integrator count rate is linearly proportional to the recorder scale reading. The recorder should operate at a chart speed of 1/2 inch per minute.

4. When the column temperature is stabilized at 110°C, a hydrazine sample of approximately 10 $\mu\ell$ is injected. Usually one or two injections are sufficient to condition the column as shown by reproducibility of the analysis.

5. When conditions are stable, the column conditioned and the attenuation set to the desired position, dependent upon the estimated sample concentration, the instrument is then ready for analysis of samples.

6. Inject approximately .5 $\mu\ell$ sample of the unknown hydrazine mixture. The peaks are counted and recorded as they appear. The analysis requires approximately 7 minutes and an additional 10 minutes is allowed before the next analysis to insure complete return of recorder to baseline. From three to five determinations of each sample are usually sufficient for accurate analysis.

7. The composition of the unknown mixture is estimated and the reciprocal response ratios from a mixture of similar composition is obtained from Table I and used to calculate the percent composition. This value is further refined for greater accuracy by the following steps.

a. From the calculated percent composition a similar mixture is prepared using hydrazines of known composition as determined by the acidimetric analysis (Appendix A) or equivalent method.

b. This prepared sample is then analyzed as described in step 6. From the analysis the reciprocal response ratios are determined as described in the calculation section.

c. The average relative response ratios obtained are then used to calculate the percentage composition of the unknown sample.

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4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

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A gas chromatographic procedure is described for the analysis of a mixture of hydrazine, monomethylhydrazine (MMH) and water.

Analyses were obtained by the use of a Perkin-Elmer Vapor Fractometer Model 154-C with a Leeds and Northrup recorder and an Instron integrator. A column packed with 10 percent Dowfax 9N9 on Teflon 6 was used. The elution of the peaks required about 7 minutes and the peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within ± 0.5 ~~percent~~ % of the amount of the individual components present in a synthetic mixture. The synthetic mixture was prepared from materials which had been analyzed by the acidimetric method. (U)

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Gas Chromatographic Analysis of Hydrazine, Monomethylhydrazine and Water in Mixed Hydrazine Fuels (U) by Richard M. Jones. China Lake, Calif., NOTS, August 1965. 20 pp. (NAVWEPS Report 8788, NOTS TP 3882), CONFIDENTIAL.

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Subj: NavWeps Report 8788 (NOTS TP 3882) Gas Chromatographic Analysis of Hydrazine, Monomethlydrazine and Water in Mixed Hydrazine Fuels, dated August 1965; transmittal of errata sheet for

Encl: (1) Errata sheet dated 3 March 1966 for subject report

1. It is requested that the corrections described on the enclosed errata sheet be incorporated in NavWeps Report 8788, NOTS TP 3882.

C. E. VAN HAGAN

NAVWEPS Report 8788
NOTS TP 3882

ERRATA

Page 16, paragraph 1 under Procedure, line 2: delete "3" and replace it with "10"

Page 16, paragraph 2 under Procedure, line 2: delete "0.20 to 0.25" and replace it with "0.10 to 0.15"

Page 16, paragraph 2 under Procedure, line 4: delete "Allow the solutions to stand approximately 30 minutes."

Page 16, paragraph 3 under Procedure, lines 1 and 2: delete "red end point with 0.5N HCl. After 10 minutes again titrate to the red end point." and replace it with "first change in the red color to a lighter red or clear with 0.5N NaOH."

Page 17, paragraph 4 under Calculations, formula change: delete

$$\frac{\text{ml (HCl) x N (HCl) x mol wt (hydrazine)}}{\text{10 x sample weight in grams}}$$

and replace it with

$$\frac{\text{(ml HCl x N HCl) - (ml NaOH x N NaOH) x mol wt (hydrazine)}}{\text{10 x sample weight in grams}}$$

9 March 1966
Enclosure (1)